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DIFFERENT Pd-ZnO INTERFACES STUDIED WITH HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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Introduction

Metal-oxide interfaces are important in many technical applications, ranging from laser cladding of metals to electronic chip packaging. With the advent of ultra high resolution transmission electron microscopy it became possible to unravel the structural properties of these interfaces at an atomic scale. In contrast to the vast amount of work on interfaces between similar crystallographic structures, i.e. cube-on-cube, in this study we look at an interface between an fcc metal (Pd) and an hcp oxide (ZnO) at an atomistic scale using high resolution electron microscopy (HRTEM). Palladium was chosen as metal because it has a rather high stacking-fault energy compared to silver which was used in a previous study [1]. Furthermore, the lattice constant of Pd (0.389 nm) is between those of silver and copper, both observed in combination with ZnO before. Comparing different metals in combination with the same oxide gives the opportunity to study the influence of material properties like the stacking fault energy and shear modulus on the morphology of the precipitates and the structure of the interfaces.

Zinc oxide is known to exist in three phases, the stable wurtzite or hcp form, a metastable sphalerite (zinc-blende) structure [2] and in a high pressure rock-salt structure [3]. The sphalerite structure can be regarded as a transformed wurtzite structure, analogous to the transformation of hcp to fcc. According to Hartree-Fock calculations [4] the energy difference between wurtzite and sphalerite is only 0.05 eV per formula unit.

Experimental Procedures

Palladium sheet 200 μm thick was cold-rolled to 100 μm to provide the right texture for HRTEM imaging. Palladium was alloyed with zinc by diffusion of zinc vapour into the 100 μm thick Pd sheet at 1273K for four days in an evacuated quartz tube. After the diffusion treatment the alloy is internally oxidised for 17h at 1073K in air. Two alloys were made with respectively 1 and 2 weight percent zinc, equal to 1.6 and 3.2 atomic percent zinc. Preparation of the specimens for HRTEM observation was done by dimpling and subsequent ion-milling down to electron transparency. Microscopy was performed with a JEOL 4000 EX ii electron microscope with 0.165 nm resolution at 400kV.

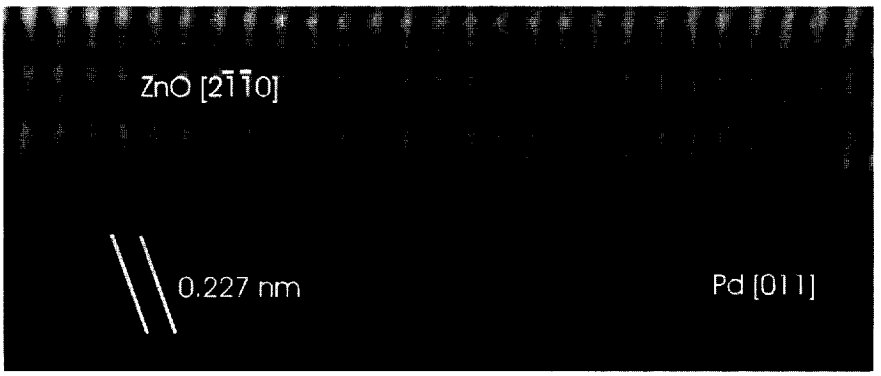

Figure 1. Pd-ZnO basal plane interface.

Observations

The average size of the plate-like precipitates is around 1 μm with a thickness of about 100 nm. The majority have a truncated trigonal shape, with large {0001} basal plane facets parallel to {111} planes in Pd and the [11$\bar{2}$0] direction in ZnO parallel to the [110] direction in Pd (OR1). This orientation relation is also the most common in Ag-ZnO and Cu-ZnO. The ends of the precipitates are in general more rounded off compared to ZnO precipitates in Ag, with some facets along the first pyramidal and prismatic planes. Because the sample was not homogenised before oxidation the concentration of zinc and the amount of precipitates after oxidation varies from grain to grain. An interesting observation was that there were many edge dislocations visible in the interior of some ZnO precipitates. One precipitate was encountered with a different orientation relation, $(002)_{Pd}//(0\bar{1}\bar{1}1)_{ZnO}$ and $[011]_{Pd}//[2\bar{1}\bar{1}0]_{ZnO}$.

A picture of the basal plane interface is shown in Figure 1. The ZnO is imaged along a $\langle 11\bar{2}0\rangle$ direction and the Pd is imaged along $\langle 110\rangle$. At the interface no relaxation of the metal or oxide is visible like the findings of Ichinose et.al. [5]. However, apart from the basal plane interfaces obviously some other planes of the ZnO system are in contact with Pd and have some interesting features. One example of an other type of interface is shown in Figure 2. It is an (200) plane of Pd in contact with a facetted

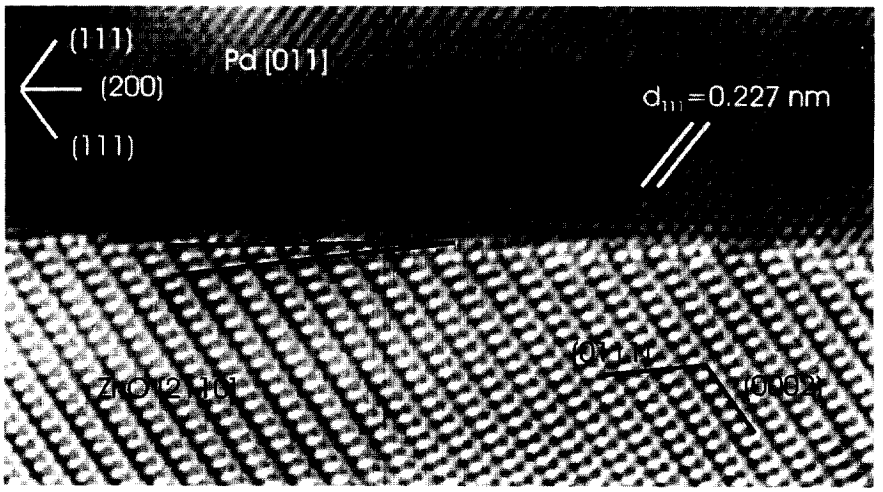

Figure 2. First pyramidal plane of ZnO in contact with Pd (002). The angle between the two planes is about 6.5°.

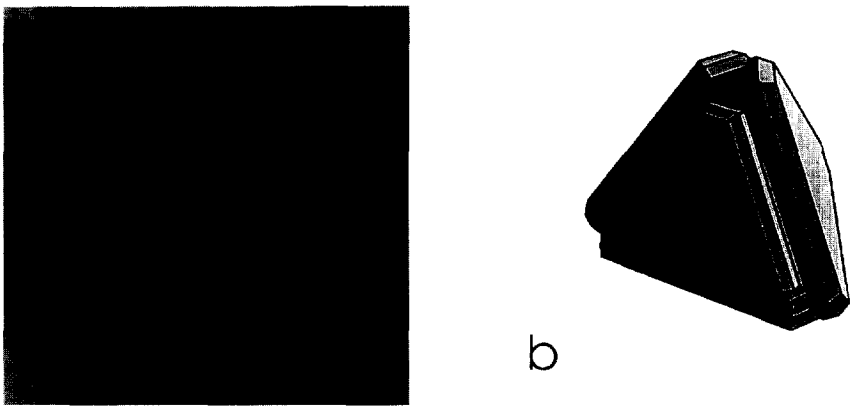

Figure 3. a) Typical sphalerite-wurtzite configuration. Because of the thinning of the sample only two of the wurtzite plates are visible. b) Probable 3-D configuration of the precipitate.

$[0\bar{1}11]$ ZnO plane. Interesting is that the oxide is stepped rather than the metal. From this picture it is clear that the $(1\bar{1}1)$ plane of Pd is still parallel to the (0002) plane in ZnO, implied by the orientation relation. The first pyramidal $(0\bar{1}11)$ plane of ZnO must have an angle of 6.84° with the (200) plane in Pd; this can geometrically be described by $(2\bar{1}\bar{1}0)$ type ledges with $[11\bar{2}0]$ type steps in the plane of projection. One precipitate has been found with an orientation relation with $(002)_{Pd}//(0\bar{1}11)_{ZnO}$ and $[011]_{Pd}//[2\bar{1}\bar{1}0]_{ZnO}$. Unfortunately there is only one picture of an interface with a {111} plane of Pd available.

Beside these wurtzite precipitates also some precipitates occur that contain both sphalerite and wurtzite ZnO. A picture of such a tetrahedral precipitate is shown in Figure 3a. It is made up of four wurtzite ZnO platelets which form a tetrahedron and a nucleus of sphalerite ZnO. This configuration is also found in Ag-ZnO by Vellinga [1]. A schematic 3D picture of the arrangement of the four ZnO platelets is shown in Figure 4. A detailed picture of a 'triple' point of two wurtzite plates and the sphalerite nucleus is shown in Figure 3b. The wurtzite ZnO fits perfectly onto the sphalerite ZnO, whereas the two wurtzite plates have a near-perfect twin plane interface which can be explained by the c/a ratio for wurtzite ZnO. Also two rather large (300 nm) tetrahedral precipitates were found that consisted only of sphalerite ZnO. One precipitate was found that consisted of two tetrahedral wurtzite/sphalerite configurations that have grown together during nucleation. Between these two there is a small amount of sphalerite ZnO that apparently has formed after nucleation.

Discussion

Wurtzite ZnO

For the basal plane in contact with a {111} plane of Pd it is most likely to find a interface structure with trigonal symmetry as found for Cu-MgO interfaces [7–8]. However, no clear contrast variations are found that point to such a network. This probably means that the displacements are too small to be observed. In the Ag-ZnO samples and Cu-ZnO samples also no contrast variation is observed along the basal plane interface [1].

The stepped oxide interfaces can be explained by looking at the shear moduli of the materials, 53 GPa for Pd and 46 GPa for ZnO [10] (wurtzite). This is a rather even distribution compared to the majority of metal-oxide systems where the oxide can be regarded rigid compared to the metal. When

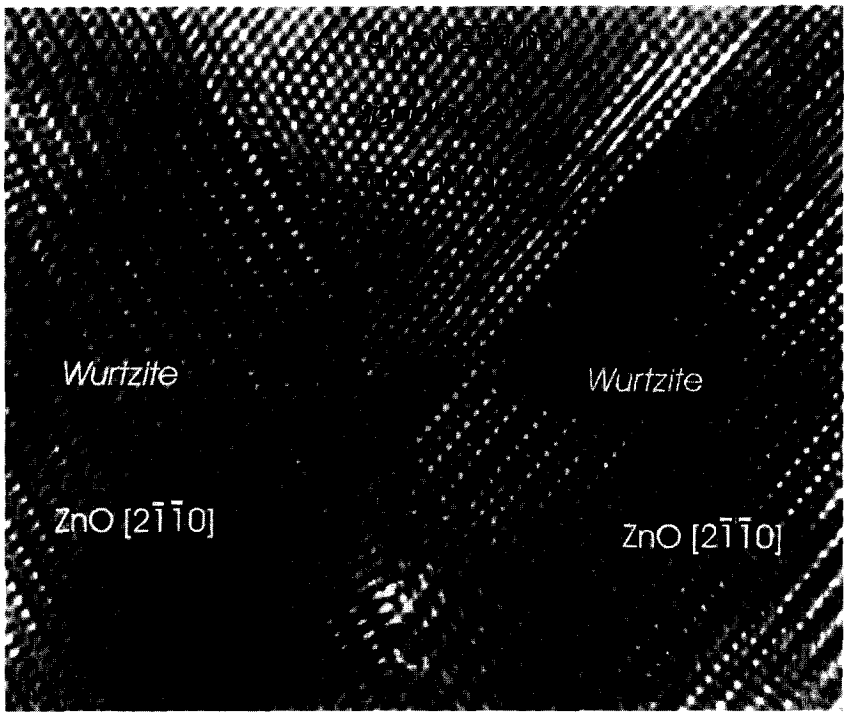

Figure 4. Picture of a 'triple point' between two wurtzite platelets and the sphalerite nucleus. Note the perfect match between the sphalerite and the wurtzite.

we compare Pd-ZnO with the Ag-ZnO system no stand-off dislocations are formed to relieve the small tilt of the interface. This can be explained by the high stacking fault energy of palladium (180 mJ/m^2) compared with silver (17 mJ/m^2) [9] since the stand-off dislocations leave a stacking-faulted area behind in the metal [1]. Another effect that might explain the preference of $(200)_{Pd}$ planes is the occurrence of some precipitates with a differing orientation relation. The (200) planes of the metal are exactly aligned with $\{01\bar{1}1\}$ planes in ZnO. This would mean that the {200} of Pd is also a low energy plane in contact with Pd.

Sphalerite ZnO

Because a substantial amount of precipitates were found that contained a mixture of sphalerite and wurtzite ZnO we believe that in some cases ZnO nucleates in the sphalerite form. This can be explained by the small energy difference between the two phases and the surrounding of the ZnO which is a fcc metal. The tetrahedral shape of the sphalerite precipitates, in contrast to the octahedral shape of MgO in Pd [6], can be explained by the tetrahedral instead of octahedral surrounding of the oxygen atoms in ZnO. After the precipitate has grown to a certain size it becomes more favourable for the sphalerite to transform or to continue growth as wurtzite ZnO on the four tetrahedral planes, providing the right 'epitaxy' for the sphalerite and a (low energy) basal plane in contact with the metal. In some grains most of the precipitates contained sphalerite which means that for some particular oxidation parameters sphalerite nucleation is favoured over wurtzite nucleation. These parameters are however not known on a microscopic scale. The two tetrahedral precipitates that have grown together show that sphalerite may also be formed when two wurtzite planes meet. The difference between nucleation as sphalerite and

later formation of sphalerite is visible by the 'wetting angle' between the sphalerite and the wurtzite 'substrate' that shows that the sphalerite appeared later.

Conclusions

Compared to Ag-ZnO and Cu-ZnO the Pd-ZnO system has some different features. Pd-ZnO interfaces where a Pd {200} plane is involved and a small tilt are compensated by steps in the oxide rather than the metal. This is also reflected in a orientation relation that deviates from the standard orientation. It also means that after Pd{111} planes the Pd{002}is lowest in energy when in contact with ZnO. Common to both Ag-ZnO and Pd-ZnO is that ZnO sometimes nucleates in the sphalerite structure due to the small energy difference between sphalerite and wurtzite and the surrounding metal with a fcc structure. A detailed study of the interfacial dislocation structures is still underway as well as the influence of segregates on the precipitates.

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